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<b>(21) International Application Number:</b> PCT/EP93/03355 <b>(22) International Filing Date:</b> 26 November 1993 (26.11.93)  <b>(30) Priority Data:</b> 9224876.4 27 November 1992 (27.11.92) GB  <b>(71) Applicant (for all designated States except US):</b> EXXON CHEMICAL PATENTS INC. [US/US]; 1900 East Linden Avenue, Linden, NJ 07036 (US).  <b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only):</b> CHAMBON, François, Henri [FR/BE]; Rue de Tulipe 2, B-1950 Kraainem (BE). TRUDELL, Barry, Colin [CA/US]; 16019 Greenwood Pines, Houston, TX 77062 (US).  <b>(74) Agents:</b> VELDHUIZEN, Albert, Dirk, Willem et al.; Exxon Chemical Limited, Exxon Chemical Technology Centre, P.O. Box 1, Abingdon, Oxfordshire OX13 6BB (GB).		<b>(81) Designated States:</b> CA, JP, US, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> IMPROVED PROCESSING POLYOLEFIN BLENDS  <b>(57) Abstract</b>  Using effective amounts of low weight-average molecular weight polyethylene having a density greater than or equal to 0.900 g/cm <sup>3</sup> in polyolefin blends such as to have a blend polydispersity index of greater than 3.5 are shown to achieve improved surface properties after higher shear processing of the blends, largely eliminating or effectively minimizing the occurrence of surface distortions.		

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**TITLE: Improved Processing Polyolefin Blends**

**Technical Field**

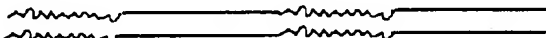
This invention relates to polyolefin blends capable of high shear extrusion into extruded compositions exhibiting improved surface properties of gloss and smoothness. More particularly, it relates to polyolefin blend compositions containing from about 30 wt.% to about 80 wt.% low weight-average molecular weight polyethylene having a density greater than or equal to  $0.900 \text{ g/cm}^3$ , and having a blend polydispersity index of greater than 3.5.


**Background of the Invention**

Flow instabilities in polymer processing often dramatically limit the maximum throughput possible in common converting operations. They produce irregularities of the polymer surface which are generally referred to as "melt fracture". Depending on the periodicity and the amplitude of the distortion, they can be classified as : slip-stick, sharkskin and wavy fracture. Slipstick is an observed result of the phenomena that at characteristic throughput-pressure required to extrude the resin, the pressure often begins to oscillate. Under oscillating pressure conditions, the extrudate exhibits alternating regions of smooth and rough surface making it of essentially no use. Over the recent past, slip-stick has been a very severe limiting factor for the wide utilization of neat polyethylene resins based upon LLDPE. Sharkskin is shear-stress induced surface irregularity of high frequency and low magnitude that reduces surface gloss, increases apparent roughness and accordingly limits the use of the compositions or limits the processing conditions such that the process is not commercially attractive. Numerous patents have addressed these phenomena, e.g. US-A-4 859 398 discloses extrusion

process parameters that are said to reduce sharkskin. However, this description also indicates that shear-stress and exit die temperature are to be kept at low values, thus limiting the utility of such solutions.

The following visual representation illustrates examples of the surface characteristics of extrudate having slip-stick and sharkskin :

Slip-stick 

Sharkskin 

In view of these problems with processing and resulting surface properties, various processing aids and/or flow improvers have been utilized or proposed. See generally, Ency. of Poly.Sci. and Eng. (2d Ed.), Index vol., pp. 307-324 (J. Wiley & Sons, 1990). Polyethylene wax is listed as a lubricating processing aid for LLDPE on p. 320. However these additives can lead to other problems because of their general incompatibility with the polyolefin resins being processed. Traditional processing aids such as silicone oils and other low molecular weight, non-hydrocarbon compounds are often prohibited from use in medical and food packaging applications. Additionally, the use of the traditional low molecular weight compounds can cause "blooming", the exudation of the low molecular weight materials during use or storage over time, which results in an oily feel or even discoloration of the final extruded compositions.

Additionally it is known generally for polyolefin polymers that the use of broad molecular weight distribution (MWD, or polydispersity index) blend compositions can allow increased processing speeds while maintaining or improving various properties, including surface properties. In particular, PCT-A-WO 90/03414 (and

surface properties. In particular, PCT-A-WO 90/03414 (and corresponding U.S. application number 07/916,738) addresses a broad class of linear ethylene interpolymer blends having improved mechanical, physical or chemical properties wherein the blends have  $M_w/M_n > 3$  and wherein each blend component has a higher comonomer content than any other component of lower average molecular weight (described as a narrow composition distribution having composition distribution breadth index, "CDBI", of  $>50\%$ ). Samples 9D, 21F and 22E of Example 3 illustrate blends having approximately 33wt.% of a polyethylene blend component having 0.0wt.% comonomer and  $M_w$  of 13,400. Though, in general, poor surface properties are said to be minimized, and improved properties of reduced coefficients of friction and lower extractables are said to be achieved by the broad class of interpolymer blends described, the examples address only compression molded sheets and the properties thereof, not including extrudate properties.

Additionally, in co-pending U.S. application number 07/817,701, not published as of the date of the filing of this case, polyolefin blends shown to have improved heat sealing properties are described. These blends are described to comprise A and B components wherein the A component is linear ethylene interpolymers said to have a density of from 0.86 to 0.96 g/cm<sup>3</sup>, and may include high density polyethylene with density above about 0.940 g/cm<sup>3</sup>; a weight average molecular weight of  $10^3$  to  $10^6$ ; and, preferably having a CDBI  $>50\%$ . The B component is said to include any of the traditional polyethylene copolymers known in the prior art. It is disclosed therein that by formulating blends of differing molecular weights of the A interpolymers to make up the A component such properties as tear strength, modulus, yield strength, clarity, gloss, haze, and heat sealability may be retained as with the individual interpolymers, or improved. The description addresses heat-sealable

articles and the examples address films having improved heat-sealing performance, extrudate properties are not described.

The effects of higher speed melt processing have also been recently addressed in the technical literature. Extrudate surface defects in linear polydimethylsiloxane are addressed by simulation methods to postulate that hydrostatic tension cavitates the polymer melt within 1 micron of the die exit to create conditions for sharkskin formation in "Sharkskin defects of polymer melts: The role of cohesion and adhesion", B. Tremblay, J. Rheol. 35 (6), pp. 989-975 (August, 1991). The author also postulates, p. 997, that the known phenomena of decreasing sharkskin with increase of MWD may possibly be explained by the diffusion of low molecular weight species and filling of microscopic voids produced so as to prevent cavitation. In "Effects of Polymer Structure on the Onset of Processing Defects in Linear Low Density Polyethylene", L.Kale et al, Poly. Eng. and Sci., v.31, no. 22 (Nov. 1991), it was concluded that the severity of the melt processing defects appears to be inversely related to the amount of low molecular weight, highly branched material.

### Figures

FIG. 1 is a graphic plot of the measurement of amplitude of distortion against shear rate for Examples 1 and 2 blends in accordance with the invention and comparison examples A and B blends representing the prior art.

### Invention Disclosure

It has been discovered that by using effective amounts of a low weight-average molecular weight thermoplastic polyethylene having a density greater than or equal to 0.900 g/cm<sup>3</sup> ("PE modifier") in polyolefin blends and that by achieving a blend polydispersity index

of greater than 3.5 for the resulting blends, surface properties resulting from high shear processing of the blends are improved by largely eliminating or effectively minimizing the occurrence of surface distortions. Thus the invention is directed to a polyolefin blend suitable for high shear-stress extrusion characterized by comprising : a) at least 30 wt.%, particularly more than about 45 wt.%, or even 60 wt % and higher, to about 80 wt.% of total polymer blend of low  $M_w$  polyethylene having a density greater than or equal to  $0.900 \text{ g/cm}^3$ ; and, b) 70 to 20 wt.% of total polymer blend at least one of ethylene homopolymers or copolymers wherein the ethylene content is at least 70 mol.%, preferably at least 80 mol.%, where  $C_3$ - $C_{16}$   $\alpha$ -olefins are copolymerized, and wherein the M.I. of the b) component is selected such that the blend of a) and b) exhibits an MWD of greater than 3.5.

By means of the present invention, surface distortion of polyolefin extrudate is controlled in two ways :

- it is eliminated or at least shifted outside the processing window, thus making the region of higher extrusion rates practically useful ;
- it can be finely tuned so that slip-stick is eliminated while surface distortion of low amplitude is retained. This is in recognition of the fact that for some applications surface distortion may be desirable, i.e. light sharkskin provides non-glossy, improved feel extrudates.

Accordingly, increased processing speeds are made possible for applications of polyolefin extruded products where surface defects or distortions were previously detriments to the desired end use. Also means provided for selecting the polyolefin blends of the invention permit tailoring of blend melt index ("M.I.") to achieve M.I. ranges that will be most suitable for existing equipment to maximize processing speeds while avoiding

the surface distortions previously observed at such speeds on that equipment.

#### Best Mode and Examples of the Invention

The invention will typically comprise the use of about 30 wt.% to about 80 wt.% of the PE modifier of the invention in a polyolefin blend, which with the provision of said PE modifier has a polydispersity index of  $> 3.5$ , for the purpose of improving the surface distortion of polyolefin blends subjected to high shear rate extrusion. Alternatively, the invention can be defined as a process for producing an extruded polyolefin composition having improved surface properties of gloss and smoothness characterized by comprising the steps of a) providing a polyolefin blend comprising at least about 30 wt.% to about 80 wt.% PE modifier and having a blend polydispersity index of greater than 3.5; and, b) extruding the blend of step a) under high shear conditions.

For the purposes of describing the invention and results of its use the term surface roughness index ( $R_A$ ) is defined to mean the first moment of the amplitude of surface distortion as measured by a SURFCOM 110B, from TOKYO SEIMITSU CO. Ltd., Tokyo, Japan, and expressed in units of micrometers ( $\mu\text{m}$ ). Typically the  $R_A$  of polyolefin blends extruded under the higher shear rate conditions of the invention will be less than  $10\mu\text{m}$ , preferably less than  $9\mu\text{m}$ , and even more preferable less than  $3\mu\text{m}$ . The term "high shear rate extrusion" in the description of the invention is meant as understood in the polymers processing and converting art and is to encompass shear rate of not less than  $500\text{ s}^{-1}$  (second<sup>-1</sup> or 1/second), for example,  $500\text{--}1900\text{ s}^{-1}$ , and above. Melt index (M.I.) as referred to in the description and claims refers to that measured in g/10 min. at  $190^\circ\text{C}$  and 2.16 kg (ASTM D1238). Density is reported in  $\text{g/cm}^3$ .



The PE modifier of the invention is one having a low weight-average molecular weight ( $M_w$ ), typically characterized by an M.I. greater than or equal to 50 but less than or equal to 1000, preferably from 100 to 650, and a density of at least 0.900 g/cm<sup>3</sup>, preferably from 0.910, more preferably from 0.920, up to about 0.945 or even up to 0.975. It will be comprised of polyethylene homopolymer or copolymer, or blends, of ethylene and one or more monomers copolymerizable therewith, having sufficient degree of crystallinity to achieve the density range described. Preferred copolymerizable monomers include the C<sub>3</sub> - C<sub>16</sub>  $\alpha$ -olefins or diolefins, particularly the C<sub>4</sub> - C<sub>8</sub>  $\alpha$ -olefins. Level of incorporation of the comonomers determines density variation and can be either random or more regular. The density limitations are critical to the invention in that incorporation of the copolymerizable monomers disrupts the crystalline order of the copolymer formed, due to creation of branching in the otherwise linear ethylene-based polymer, and thus operates to decrease the apparent density with increased comonomer incorporation.

Methods of preparation of the PE modifier of the invention are well-known in the art. One method is in PCT-A1-WO 90/03414, which is based upon U.S. application Ser. No. 252,094 filed 30.09.88, the disclosure of which is incorporated by reference for purposes of U.S. patent practice. Catalysts and means of preparation of suitable polyethylene homo- and copolymers appear in the patent literature, see e.g., U.S. patents 4,429,079 and 4,461,873, and the co-pending U.S. application 07/817,701 which are also incorporated by reference for purposes of U.S. patent practice. Additionally, such publications as Ency. of Poly. Sci. and Eng., vol. 6, pp. 383-490 (J. Wiley & Sons, 1986), and Textbook of Polymer Science (3d ed.), F.W. Billmeyer, Jr., Pages 361-370 (J. Wiley & Sons, 1984) can be consulted for background information as to comonomers, methods of preparation and sources of

commercial products. Low  $M_w$  high-density polyethylene (HDPE) is suitable and can be prepared by metal-catalysed coordination polymerization, typically with either a co-catalyst system based on one or more transition metals and one or more of an aluminum alkyl or aluminum haloalkyl or by supported metal oxide compositions, and more recently by metallocene catalyst systems. Such HDPE typically has up to about 2 wt.% comonomer, e.g. 1-butene, 1-hexene or 1-octene. Inclusion of more, up to about 10 wt.%, results in polyethylene copolymer having densities less than about 0.941 g/cm<sup>3</sup> but still within the density range defined for the purposes of this invention.

The polyolefin blend of the invention comprises, in addition to the PE Modifier of the invention, at least one of ethylene homopolymers or copolymers, as defined above, wherein the ethylene content is at least 70 mol.%, preferably at least 80 mol.%, where C<sub>3</sub>-C<sub>16</sub>  $\alpha$ -olefins and/or diolefins are copolymerized, and the M.I. is less than 50, preferably less than 10, more preferably less than 3. This polyolefin blend may comprise any one or more of LLDPE, ULDPE, or LDPE as those terms are understood in the art and appear in such as Ency. of Poly. Sci. and Eng. and Textbook of Polymer Science, see above. Blends comprising either or both of LLDPE and VLDPE are particularly suitable. Also, HDPE can be effectively modified by the PE modifier of the invention, or included in blends so modified, so long as the HDPE is of significantly higher  $M_w$ , e.g. or having M.I. less than 10, preferably less than 3, and of equivalent or lower density than the PE modifier. Additionally these blends will encompass any of the polyethylene polymers and blends emerging from new technologies relating to metallocene coordination catalysis, such as those exemplified in the prior art description of this application, that have the monomer content and M.I. specified.

Low-density polyethylene ("LDPE") is a well-known commodity product and includes both low and medium density polyethylene having densities of about 0.910 to 0.940 g/cm<sup>3</sup>. The term as used herein includes copolymers and terpolymers of ethylene which are thermoplastic resins. Comonomers typically include C<sub>3</sub>-C<sub>10</sub>  $\alpha$ -olefins. The C<sub>2</sub> content will typically exceed about 80 wt% of the polyethylene co- and terpolymers. These polymers and copolymers are typically prepared by metal catalysed coordination polymerization in accordance with processes well known in the polymers art. A typical LDPE is available commercially as ESCORENE<sup>®</sup> LD 180 through EXXON Chemical International Marketing B.V., BELGIUM. LDPE with densities of 0.930 g/cm<sup>3</sup> and lower are particularly suitable in accordance with the invention.

The linear low-density polyethylene ("LLDPE") of the invention are copolymers of ethylene with at least one  $\alpha$ -olefin having at least four carbon atoms, e.g., 1-butene, 1-hexene, 1-octene, etc. The processes for producing LLDPE are typically based on coordination polymerization and are well known in the art. Commercial grades are widely available. A typical LLDPE is available commercially as ESCORENE<sup>®</sup> LL 6301 RQ through EXXON Chemical International Marketing B.V., BELGIUM. Preferably the LLDPE of the invention will have a density of less than 0.930.

High density polyethylene ("HDPE") has a density of about 0.941 to 0.975 g/cm<sup>3</sup> and is an established product of commerce. Suitable HDPE has molecular weights in the range of 150,000 to 300,000, and includes high molecular weight ("HMW") HDPE which has molecular weights in the range of 300,000 to 500,000. Its manufacture and general properties are well known in the art.

Blends of the invention are prepared by blending the described components in the desired proportions using conventional melt-processing blending techniques and apparatus, for example, Banbury mixers, single or

multiple screw extruders and the like. To achieve the described MWD for the invention blends, components are selected meeting the above criteria and provided in such proportions as empirically result in both of targetted M.I. and MWD for the blend as is conventionally done in the polymer processing industry. Conversion of M.I. to  $M_w$  for initial target proportions, from which iteration is conducted for fine tuning, is typically done by use of empirically derived relationships for the specific polymers as is known in the art. See, for example, "Melt Flow Index : More Than Just A Quality Control Rheological Parameter. Part I." , A. Shenoy and D. Saini, Advances in Polymer Technology, Vol. 6, No. 1, 1-58 (1986).

Alternatively, blends may be made by direct polymerization, using, for example, two or more catalysts in a single reactor or one or more catalysts in parallel or series reactors, where the catalysts, monomer feeds, and reactor conditions are provided that are suitable for the preparation of polymer components meeting the invention description. Such direct polymerization blends are known in the polyolefin art, see for example PCT-A-WO 90/03414. The disclosures addressing polyolefin blends of both of U.S. application Ser. No. 252,094 filed 30 September 1988 and U.S. application Ser. No. 07/817,701 filed 7 January 1992 are incorporated by reference for purposes of U.S. patent practice.

By use of the invention, the rate of surface roughness increase of the extruded polyolefin compositons with extrusion throughput can be accurately controlled by the extent to which MWD is broadened and the difference in density, between the PE Modifier and remaining polyolefin component, is increased. More specifically, based on the present invention, resins with comparably useful MIs can be tailored by selection of component M.I. and density such that  $R_A$  remain constant over a wide range of extrusion rates. In Examples 1 and 2, below, increasing the difference in measured densities between

the PE Modifier and the other polyolefin component decreased the measured  $R_A$  in addition to flattening for both the curve of  $R_A$  vs. shear rate, see Fig. 1.

Without intending to be present limitations to the invention, it is believed that the presence of the PE modifier in the polyolefin blends of the invention permits the improved processing with decreased surface defects due to a migration of at least an effective amount of the PE modifier to the surface of the blend during the high shear stress processing. Both of the low  $M_w$  and the low levels of chain branching, as is reflected in the density, permit improved dispersion and ease of migration to the surface. However the fact that the PE modifier is still of a high enough  $M_w$  to permit of some level of chain entanglement likely prevents its being significantly extractable and helps prevent reduction of blend viscosity below that typically necessary for effective extrusion.

In conclusion, the combination of the density effects and MWD described in the present invention will allow the polymer manufacturer to design resins which can be processed at unusually higher converting rates retaining simultaneously a complete control over the surface aspect of the extrudate. It will be apparent to those of skill in polymer science given the disclosure herein that the principles of this invention will be extendable to other polymer systems, that is inclusion of one, or more, miscible polymer species that is of lower molecular weight and higher in density than the matrix polymer or polymer blend to be processed by extrusion will enable improvement of the surface appearance and smoothness.

The industrial applicability of this invention will arise principally in the polymer processing and converting industry where polyolefin films, laminations, coatings, extrusion molded parts and articles, injection molded parts and articles, and the like, are made. Particular advantage can be obtained for those

applications where the traditional use of process aids or flow improvers was needed to utilize high shear rates, with the instant invention such process aids or flow improvers can be essentially eliminated or minimized, if not altogether omitted. For example, in blown film applications the desired shear rate for processing can be 500-1,000  $\text{s}^{-1}$ , in film casting and coating up to 2000  $\text{s}^{-1}$ , and cable coating up to 10,000  $\text{s}^{-1}$ . As with other polyolefin blends, additives such as reinforcing fillers, pigments or colorants, UV stabilizers, antioxidants, etc., can be provided in conventional amounts in accordance with conventional methods to achieve specifically desired end product properties.

The following examples are presented to illustrate the foregoing discussion. All parts, proportions and percentages are by weight unless otherwise indicated. Although the examples may be directed to certain embodiments of the present invention, they are not to be viewed as limiting the invention in any specific respect.

#### Example 1

A blend of polyolefin resin and PE modifier in accordance with the invention was provided in which the polyolefin constituted 30 wt.% and was a polyethylene copolymer resin with 20 mol.% 1-butene, having a M.I. of 0.14 and a density of 0.876, and the PE Modifier was a polyethylene copolymer, with 4 mol.% 1-butene, having a M.I. of 122 and a density of 0.925. The polydispersity of the blend as measured by GPC was 4.3 and the M.I. was 5.2. Both polymers were prepared separately by gas-phase polymerization utilizing bis(n-butylcyclopentadienyl)zirconium dichloride with alumoxane-treated silica as described for Example II of co-pending U.S. application 07/817,901 filed 7 January 1992.

Generally speaking, the M.I. of both the ethylene copolymers prepared were controlled by adjustment of the amount of  $\text{H}_2$  present and the density was controlled by

the amount of comonomer present, both during polymerization. In particular, the polymerization was conducted for the PE Modifier in a continuous gas-phase reactor at a temperature of 145°C., pressure of about  $2.07 \times 10^6$  Pa (300 psi), H<sub>2</sub> concentration 460 ppm, C<sub>2</sub> concentration 52.0 mol.% , C<sub>4</sub> concentration 2.85 mol.%. The polyolefin component was polymerized similarly at a temperature of 111.7°C., pressure of about  $2.07 \times 10^6$  Pa (300 psi), H<sub>2</sub> concentration 84 ppm, C<sub>2</sub> concentration 42.0 mol.% , C<sub>4</sub> concentration 6.45 mol.%. Residence times ranged between 2 and 5 hours. Both polymers exhibited narrow MWD (2.0-2.7) and narrow composition distribution (CD) (approximately equal comonomer content and molecular weight in each polymer chain of each component respectively).

The blend components were fed to a Werner Pfleiderer ZSK 57 twin screw extruder under melt processing conditions in which the processing temperature was 199°C., the extruder speed was 295 rpm and the applied torque was 91% maximum. The blend was mixed under these conditions, extruded and cut into pellets. These were fed to a Gottfert Rheograph 2002 for measurement of shear stress vs. shear rate using a circular die with L/D of 30/1 at 190°C. The extrudate of the Rheograph was collected, cooled and examined with the Surfcom 110B.

The blend of Example 1 was subjected to increase in shear stress, and accordingly shear rate, with the resulting observation that  $R_A$  remained essentially constant at about 1-2  $\mu\text{m}$  over shear rate increase from about  $100 \text{ s}^{-1}$  to about  $2000 \text{ s}^{-1}$ . Up to about  $10,000 \text{ s}^{-1}$ ,  $R_A$  steadily increased to about 10  $\mu\text{m}$ .

#### Example 2

A blend of polyolefin resin and a PE Modifier in accordance with the invention was provided in which the polyolefin constituted 30 wt.% and was a polyethylene copolymer resin with 8 mol.% 1-butene, having a M.I. of 0.09 and a density of 0.910, and the PE modifier

constituted 70 wt.% and was a polyethylene copolymer, with 8 mol.% 1-butene, having a M.I. of 97 and a density of 0.910. The polydispersity of the blend as measured by GPC was 4.6 and the M.I. was 4.7. Both polymers were prepared separately by gas-phase polymerization utilizing bis(n-butylcyclopentadienyl)zirconium dichloride with alumoxane treated silica generally as described in Example 1.

The blend components were melt processed and extruded for shear stress vs. shear strain analysis and  $R_A$  also in accordance with Example 1.

The  $R_A$  as measured in the Surfcom 110B remained essentially constant at about 4-6  $\mu\text{m}$  over shear rate increases from about 70  $\text{s}^{-1}$  to about 2000  $\text{s}^{-1}$ . From 2000  $\text{s}^{-1}$  to 4500  $\text{s}^{-1}$ ,  $R_A$  increased to about 10  $\mu\text{m}$ . See again FIG. 1.

#### Example 3

A blend of polyolefin resin and PE modifier in accordance with the invention was provided in which the polyolefin constituted 60 wt % and was a polyethylene copolymer resin with 8 mol % 1-butene, having a M.I. of 1.1 and a density of 0.910. The PE modifier constituted 40 wt % and was a polyethylene copolymer, with 8 mol % 1-butene, having a M.I. of 612 and a density of 0.910. The polydispersity of the blend as measured by GPC was 4.1 and the M.I. was 4.0. Both polymers were prepared separately by gas-phase polymerization, as described in Example 1.

The blend components were melt processed and extruded for testing as done for Examples 1 and 2.

The  $R_A$  as measured in the Surfcom 110B increased steadily from 0.2 to about 3  $\mu\text{m}$  over shear rate increase from about 60 to about 1000  $\text{s}^{-1}$ . From 1000 to 3000  $\text{s}^{-1}$ ,  $R_A$  increased essentially on a decreased slope to about 3-4  $\mu\text{m}$ .



Comparison Example A

A polyolefin blend having a narrow MWD (2.1) was prepared having an M.I. of 5.0 as a comparison for Examples 1 and 2. It consisted of two components in equal amounts (50 wt.% each), the A component was a polyethylene copolymer resin with 10 mol.% 1-butene, having a M.I. of 5.1 and a density of 0.897, and the B component was a polyethylene copolymer, with 5 mol.% 1-butene, having a M.I. of 4.6 and a density of 0.922. Both polymers were prepared by gas-phase polymerization utilizing bis(n-butylcyclopentadienyl)zirconium dichloride with alumoxane treated silica generally as described for Example 1.

The blend was melt processed and extruded for shear stress vs. shear strain analysis and  $R_A$  in accordance with Example 1.

The polyolefin blend exhibited essentially constant rate of increase of  $R_A$  from about 0.2  $\mu\text{m}$  to 20  $\mu\text{m}$  for shear rate increase from 150  $\text{s}^{-1}$  to 1900  $\text{s}^{-1}$ . The  $R_A$  at a shear rate of 500  $\text{s}^{-1}$  was 3  $\mu\text{m}$  and increasingly rapidly, FIG. 1.

Comparison Example B

A commercial LLDPE sold for moulding applications and ready processability was provided having a MWD above about 3.5, density of 0.935 and also an M.I. of 5.0. This Escorene<sup>®</sup> LL 6301 RQ LLDPE (Exxon Chem. Inter. Inc.) was similarly melt processed and extruded for shear stress vs. shear strain and  $R_A$  analysis in accordance with Example 1. The graph of FIG. 1 illustrates the rapid increase in  $R_A$  as a function of shear rate. The LLDPE exhibited essentially constant rate of increase of  $R_A$  from about 0.3  $\mu\text{m}$  to 8  $\mu\text{m}$  for shear rate increase from 190  $\text{s}^{-1}$  to 1900  $\text{s}^{-1}$ . The  $R_A$  at a shear rate of 10,000  $\text{s}^{-1}$  was about 20  $\mu\text{m}$ . This example illustrates that though lower high shear rate processing with some standard LLDPE products may yield acceptable  $R_A$ , the increase in shear rate resulted in rapid deterioration of  $R_A$ .

Although the invention has been described with respect to particular materials, means and embodiments it is to be understood that the invention is not limited to the particulars disclosed and extends to all equivalents within the scope of the appended claims.

The following subject matter is claimed:

## Claims :

1. A use of about 30 wt.% to about 80 wt.% of low  $M_w$  polyethylene having a density greater than or equal to  $0.900 \text{ g/cm}^3$  in a polyolefin blend, which with the provision of said polyethylene has a polydispersity index of  $> 3.5$ , for the purpose of improving the surface distortion of polyolefin blends subjected to high shear rate extrusion.
2. The use according to claim 1 wherein said polyethylene has a M.I. (g/10 min.,  $190^\circ\text{C}$ , 2.16 kg) greater than or equal to 50 but less than or equal to 1000.
3. The use according to claims 1 - 2 wherein said polyolefin blend comprises, in addition to said polyethylene, at least one of ethylene homopolymers or copolymers wherein the ethylene content is at least 70 mol.%.
4. The use according to any of claims 1 - 3 wherein said higher shear rate extrusion is not less than  $500 \text{ s}^{-1}$ .
5. The use according to claim 4 wherein said surface roughness ( $R_A$ ) is greater than 0 but less than  $2 \text{ }\mu\text{m}$ .
6. The use according to any of claims 1 - 5 wherein after extrusion at shear rates not less than  $1900 \text{ s}^{-1}$ , the surface distortion as measured by surface roughness ( $R_A$ ) is less than  $10 \text{ }\mu\text{m}$ .
7. A process for producing an extruded polyolefin composition having improved surface properties of gloss and smoothness characterized by comprising the steps of :

- a) providing a polyolefin blend comprising at least about 30 wt.% to about 80 wt.% low  $M_w$  polyethylene having a density greater than or equal to  $0.900 \text{ g/cm}^3$ , and having a blend polydispersity index of greater than 3.5; and,
  - b) extruding the blend of step a) at shear rates not less than  $500 \text{ s}^{-1}$ .
8. The process according to claim 7 wherein said higher density polyethylene has a M.I. (g/10 min.,  $190^\circ\text{C}$ , 2.16 kg) greater than or equal to 50 but less than or equal to 1000.
9. The process according to any of claims 7 - 8 wherein said polyolefin blend comprises, in addition to said polyethylene, at least one of ethylene homopolymers or copolymers wherein the ethylene content is at least 70 mol.%.
10. A polyolefin blend suitable for high shear-stress extrusion characterized by comprising :
- a) from 40 wt % to not more than 80 wt.% of total polymer blend of low  $M_w$  polyethylene having a density greater than or equal to  $0.900 \text{ g/cm}^3$ ; and,
  - b) 55 to 20 wt.% of total polymer blend of at least one of LDPE or LLDPE having density less than 0.930 wherein the ethylene content is at least 70 mol.%, preferably at least 80 mol.%, where  $\text{C}_3\text{-C}_{16}$   $\alpha$ -olefins and/or diolefins are copolymerized, and wherein the M.I. of the b) component is selected such that the blend of a) and b) exhibits an MWD of greater than 3.5.

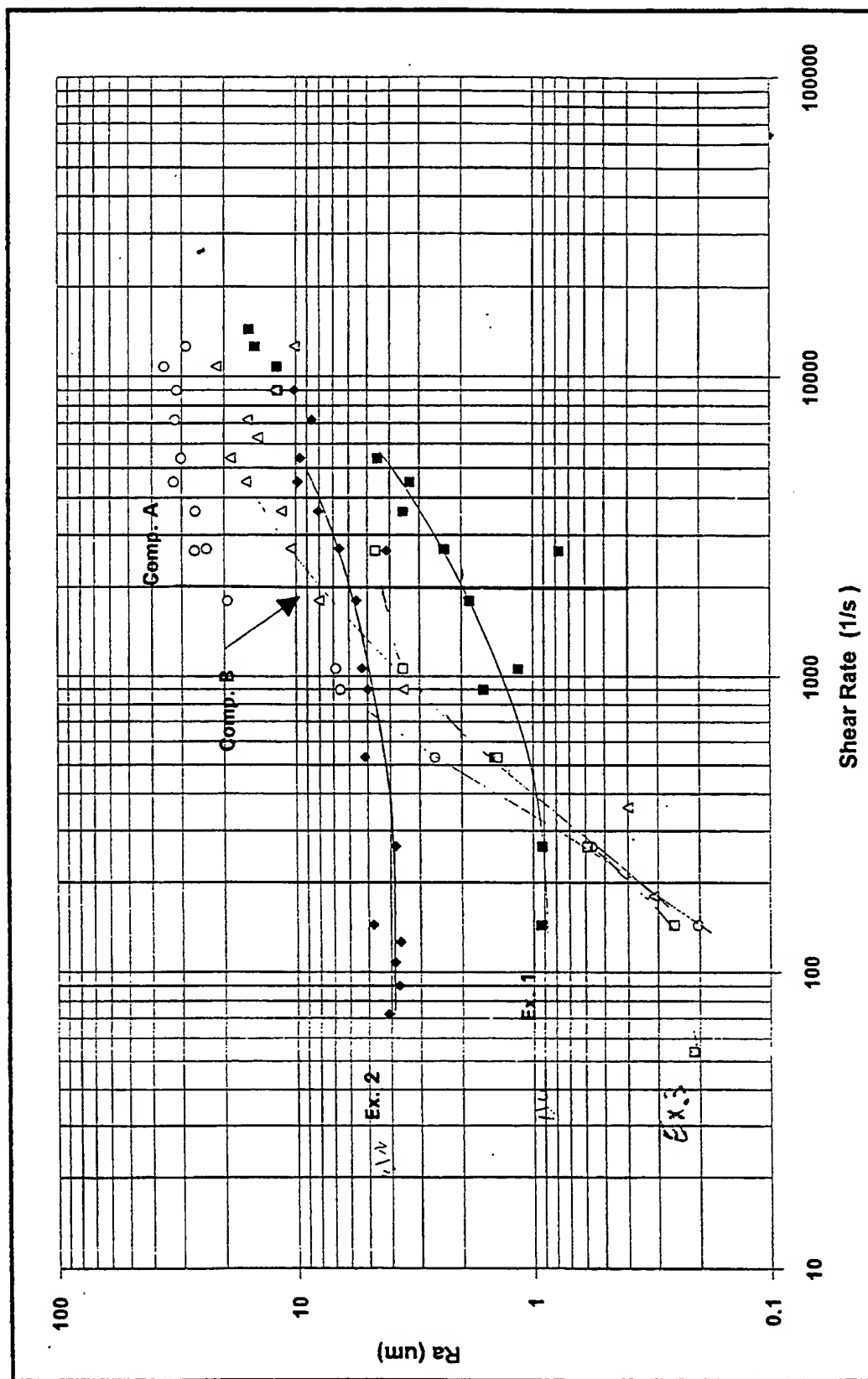


FIGURE 1

# INTERNATIONAL SEARCH REPORT

International application No.  
PCT/EP 93/03355

## A. CLASSIFICATION OF SUBJECT MATTER

IPC5: C08L 23/08

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC5: C08L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO, A1, 9003414 (EXXON CHEMICAL PATENTS INC.), 5 April 1990 (05.04.90)  -- -----	1-10

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

\* Special categories of cited documents:

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

Date of mailing of the international search report

7 March 1994

25.03.94

Name and mailing address of the International Searching Authority: Authorized officer



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